

X-ray standing wave analysis for bromine chemisorbed on silicon

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X-ray standing wave measurements on single crystals of silicon are used to determine the coverage and position of chemisorbed bromine. Detailed analysis of the position information leads to the conclusion that silicon surface atoms bonded to adsorbed bromine atoms are in extrapolated bulk-line positions. Direct measurement of the desorption of correlated bromine in air demonstrates the high stability of the Br/Si surface interface.

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I. INTRODUCTION

The x-ray standing wave technique developed by J. A. Golovchenko *et al.* has been used successfully in the past for studying the impurity correlated positions interior and exterior to the surfaces of single crystals. The interior case study was for arsenic atoms implanted and annealed to substitutional positions in silicon.¹

The exterior case study made use of the highly penetrating power of x-rays by measuring through a thin layer of methanol the correlated position of bromine atoms chemisorbed on Si(220) at the solid-liquid interface.² This Br/Si interface has proven to be an extremely stable system for non UHV analysis.³ It is the intentions of this x-ray standing wave study to quantitatively measure the stability of this interface in terms of its open air desorption rate. Also to be reported are preliminary results for the ultraviolet photon induced Br adsorption on the Si(220) surface and a surface structure characterization of the Br/Si(111) interface.

II. EXPERIMENTAL

Prior to Br deposition a $2 \times 2 \times 0.5$ cm Si sample was Syton polished and etched in hydrofluoric acid. The sample was then passed in an argon atmosphere from the HF etch to a methanol rinse and then to a 0.05% by volume Br methanol solution. While in the Br methanol bath the surface was exposed for ~5 min to uv light through a thin film of the solution. The uv source used was a 140-W low-pressure mercury vapor lamp with a quartz envelope. Following the uv Br methanol treatment four rinses in methanol were used to remove any excess Br. The sample was then blown dry in argon prior to the open air x-ray standing wave measurement.

For x-ray standing wave analysis a single crystal sample is placed in the second position of a double crystal spectrometer (Fig. 1). In the first crystal position an asymmetrically cut single crystal is used to collimate and monochromate the $\text{K}\alpha$ x-rays of a molybdenum fine focus x-ray tube ($\lambda = 0.709$ Å). As predicted by the dynamical theory of x-ray diffraction⁴ a well defined standing wave field is produced at the

second crystal when the collimated incident beam is Bragg diffracted (Fig. 2). The standing wave pattern is parallel to and has the same spacing as the Miller planes being used by both crystals for diffraction. The standing wave field extends thousands of angstroms out from the surface of the second crystal. Proper alignment of the two crystals is monitored by the angular reflectivity response of a NaI detector (Fig. 1). Currently there are a number of single crystalline materials available with mosaic spreads low enough for producing natural reflectivity curve shapes. Any of these single crystals can be used for producing a well defined x-ray standing wave field.

Advancing in angle through the strong Bragg diffraction region causes a gradual phase change of π for the amplitude of the diffracted electric field with respect to the amplitude of the incident electric field. This phase change causes the antinodes of the standing wave field to move from midway between the Miller diffracting planes to a position coincident with them. Advancing from the low angle side of the strong diffraction region to the high angle side results in increased absorption as the x-ray standing wave field antinodes approach the crystal planes. This anomalous effect accounts for the slightly nonsymmetrical shape of the reflectivity curve shown in Fig. 3. Also depicted in Fig. 3 are the x-ray field intensities for various test positions plotted as a func-

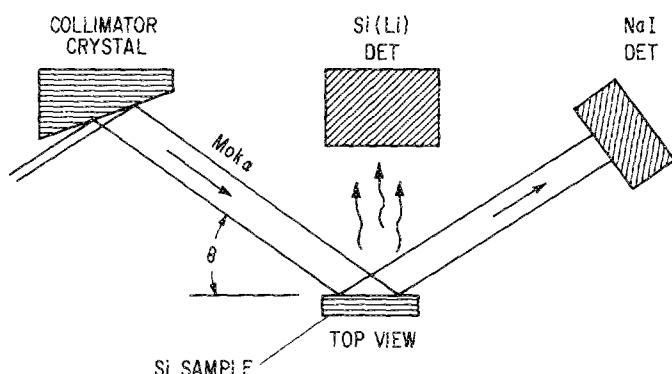


FIG. 1. Schematic layout of experimental apparatus.

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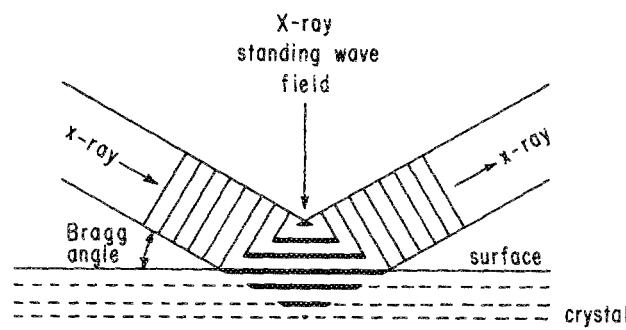


FIG. 2. Illustration of an x-ray standing wave field formed by Bragg diffraction.

tion of angle.

The inelastic interaction of the x-ray standing wave field with impurity atoms located at a particular position can be used to determine the position of these atoms relative to the diffraction planes which are generating the standing wave pattern. This positional determination is possible since the fluorescence yield from these impurity atoms is proportional to the x-ray field intensity at the impurity atom position. In our present study a Si(Li) detector (Fig. 1) is used to measure Br $\kappa\alpha$ fluorescence as the sample crystal is rocked back and forth across the Bragg reflectivity region. By monitoring the Br fluorescence yield, as a function of the relative angle between the two crystals, it is possible to determine if any sig-

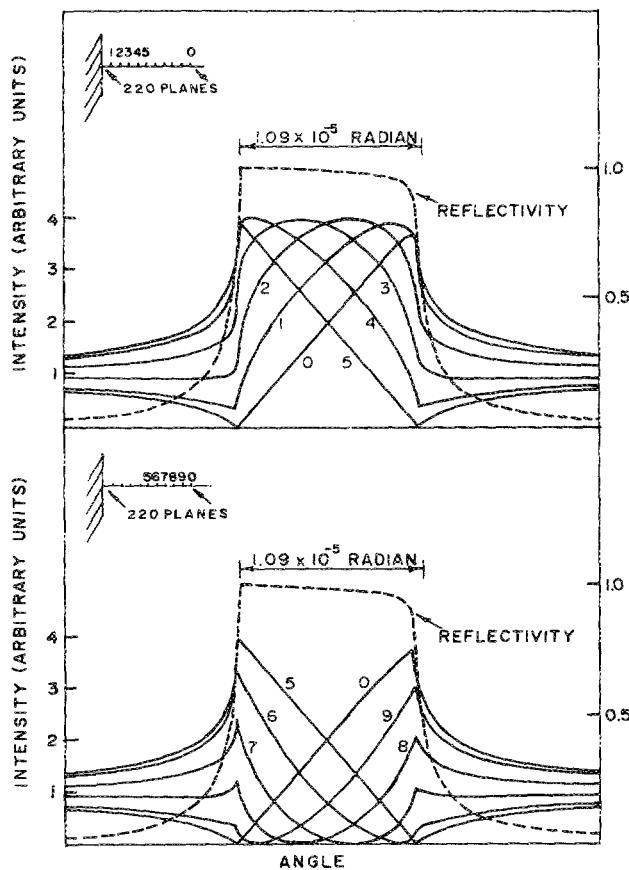


FIG. 3. —— x-ray field intensities at extended 220 lattice positions (0–9) for a perfectly collimated incident beam. ---Bragg reflectivity for a perfectly collimated incident beam.

nificant fraction of the Br atoms are positionally correlated.

For the Br/Si surface interface Br atoms are either randomly distributed (random) or take up specific preferred positions relative to the substrate diffraction planes (correlated) or a combination of these. For structure analysis the Br fluorescence yield is compared to various test position field intensity patterns (Fig. 3) variably combined with a random intensity pattern. The best fit yields the correlated position (P_C) and the fraction of Br atoms which are correlated (correlated fraction F_C). The total Br coverage (θ_T) is determined, to within a few percent, by comparing the off Bragg fluorescence yield of the chemisorbed sample to that of a standard Br implanted sample. The correlated coverage (θ_C) is then defined as the correlated fraction of the total Br coverage.

It should be noted that the correlated position for chemisorbed surface atoms is measured relative to the bulk extrapolated Si surface plane. Due to the possibility for Si surface relaxation and reconstruction, the surface plane extrapolated from the bulk and the actual Si surface may not coincide.

III. RESULTS AND DISCUSSION

For a Si (220) sample prepared as previously described, an x-ray standing wave analysis (Fig. 4) concluded that 37% of the 0.29 ± 0.03 monolayers of Br atoms on the Si (220) surface were correlated to a substrate-like fractional position of 0.93 ± 0.02 . This open air result agrees well with the previously published methanol solid–liquid interface result.² Therefore any positional perturbation due to the methanol is less than the $\pm 0.04 \text{ \AA}$ error. This open air positional measurement also agrees well with a simple model (Fig. 5), in which the surface Si atoms are assumed to have substrate-like positions and dangling bond directions. These are bonded covalently to Br atoms with a Si–Br bond length equiv-

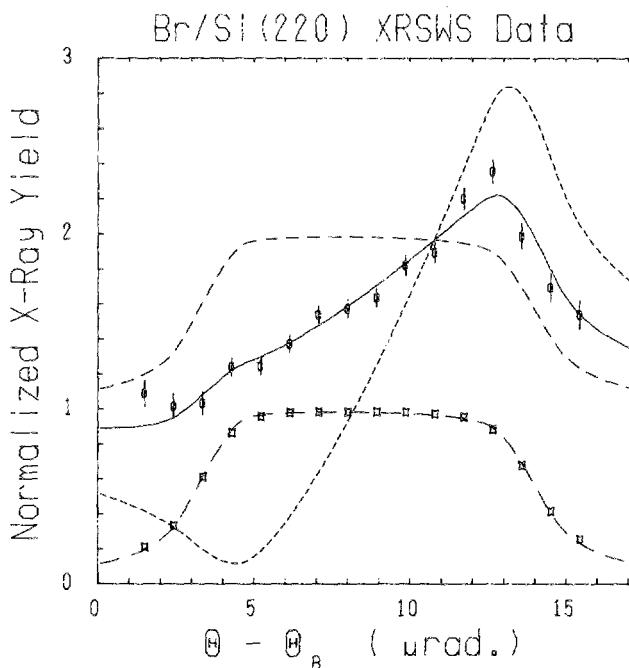


FIG. 4. ϕ Br fluorescence data; \square reflectivity data; --- Theoretical Bragg reflectivity; ... Random Theoretical yield; --- 100% correlated at $P_C = 0.93$ theoretical yield; —— 37% correlated at $P_C = 0.93$ theoretical yield.

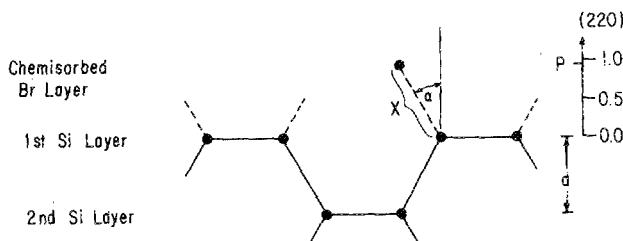


FIG. 5. Br/Si (220) substrate-like surface model $d = 1.92 \text{ \AA}$, $X = 2.17 \text{ \AA}$, $\alpha = 35.3^\circ$, $P = 0.92$.

alent to that found in SiBr_4 . This model predicts a substrate-like fractional position of 0.92. The excellent agreement between this prediction and the x-ray standing wave result is not in itself proof that all of the assumptions made in this model are correct, since the Br positional prediction of this model is made with respect to the Si surface atomic plane, while the measured result is relative to the bulk extrapolated Si surface plane. However, from electron scattering results on various silicon bromine volatile molecules,⁵ the length and angle of the Si-Br bond is known to be relatively insensitive to its neighboring environment. Therefore the only unsubstantiated assumption made in this model is that the Si surface atomic layers are bulk-like. In view of the constancy of the Si-Br covalent bond, the x-ray standing wave measurement shows that at the Br/Si (220) interface the surface Si atoms bonded to adsorbed Br are in bulk-like positions to within $\pm 0.04 \text{ \AA}$. Data taken for the adsorption of hydrogen on Si (Ref. 6) also show that when dangling surface Si bonds are saturated the surface layers relax back toward bulk-like positions.

A similar surface structure model for Br/Si (111), in which the dangling bonds are normal to the surface, predicts a Br substrate-like fractional position of 0.815. Analysis of x-ray standing wave data,⁷ that will be published at a later date, agrees with this prediction, substantiating the above conclusion that the Si surface atoms are bulk-like.

Due to the low counting rate for submonolayer coverages of Br, long time periods of angular scanning are required to

accumulate sufficient spectroscopic data in the 16 angular regions of the scan. For example, the spectroscopic scan data illustrated in Fig. 4 required thirteen hours of measurements.

Based on a number of angular scan experiments the correlated positional measurement of 0.93 has proven to be a reliable quantity. Therefore it was used as an assumed value for doing half hour measurements of the correlated coverage (θ_C). These measurements were performed by monitoring the Br fluorescence yield at only two of the previously 16 angular positions. For reasons of contrast and control the positions were taken on the two sides of the reflectivity curve, the low absorption edge and the high absorption edge. This type of a measurement will be referred to as a high/low measurement. The time development for correlated Br coverage is depicted in Fig. 6. These data show a desorption rate (k_D) proportional to the correlated coverage (θ_C):

$$\theta_C = \theta_{C,0} e^{-k_D t},$$

where $k_D = 0.050 \text{ h}^{-1}$. It is convenient in such an exponential decay curve to characterize the decay rate in terms of a decay time (half-life) which in the present case is 14 h. The Br/Si (111) interface has also shown an extremely long decay time in open air.

High/low measurements were also performed to study the effect of uv light used in the previously described sample preparation. The preliminary results indicate that samples prepared in such a manner have at least two times the amount of correlated Br as control samples which were prepared in the dark. A more complete photochemical analysis will be published at a later date.

IV. CONCLUSIONS

Since the correlated Br coverage is submonolayer and the Si (Li) detector used in this open air analysis is unable to detect oxygen and hydrocarbons, the actual complexity of the Br/Si surface interface is not completely clear from these measurements. It is possible that x-ray induced Auger emission from such surfaces in a vacuum can provide additional

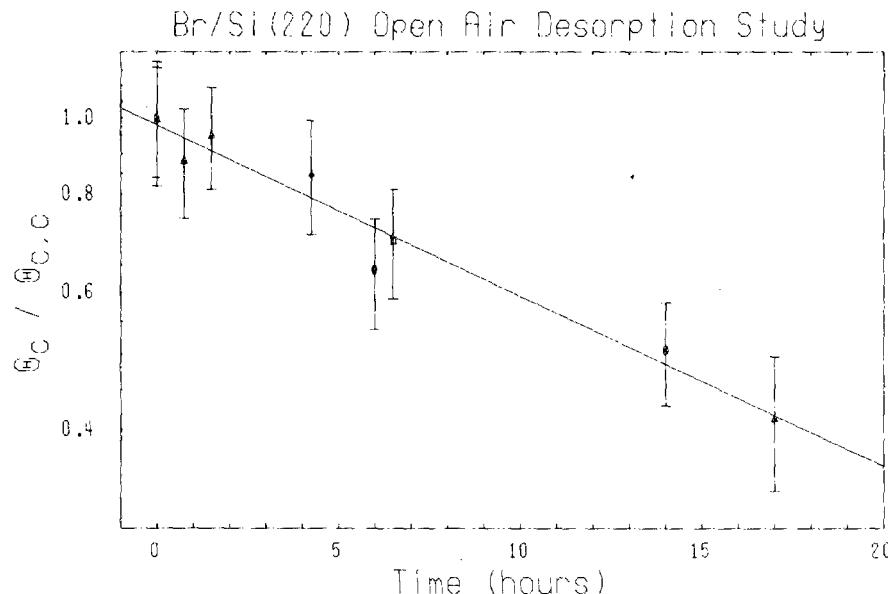


FIG. 6. Time development of correlated Br coverage (θ_C) relative to the initial correlated Br coverage ($\theta_{C,0}$). □ value from 13 h scan of Fig. 4; ○ from high/low measurements taken during scan; ▲ from a subsequent high/low analysis.

information. However, the ability of the x-ray standing wave technique to make high resolution measurements on open air or *in situ* interfaces leads to some unique results.

The existence of Br atoms correlated to substrate-like positions is evidence for a certain degree of order at the Br/Si interface, and the extremely long half-life for correlated Br atoms at this open air interface shows its stability.

The effect that this interface may have on oxidation is also of interest and presently is being studied by x-ray standing wave analysis combined with ion backscattering/channeling experiments.

Future plans for joining the x-ray standing wave technique to a synchrotron x-ray source will greatly enhance the ability for doing time developed desorption and uv induced adsorption experiments.

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